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Identification of Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate in the Los Angeles Atmosphere

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16. ABSTRACT

Analytical techniques have been developed for the collection and determination of gas phase dimethyl sulfate and monomethyl sulfuric acid based on collection of the alkyl sulfate compounds with both denuder tubes and resin sorption beds and analysis of the collected material by ion chromatography. Gas phase dimethyl sulfate and monomethyl sulfuric acid have been identified in Los Angeles using these techniques. The data indicate that dimethyl sulfate is present in both particles and in the gas phase. The concentration of gas phase methyl sulfates was found to be several μg/m^3. These species thus account for a significant fraction of the total sulfur budget in the Los Angeles Basin during the sample period.

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ES&T RESEARCH

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JOURNAL ARTICLE

Identification of Gas-Phase Dimethyl Sulfate and Monomethyl Hydrogen Sulfate in the Los Angeles Atmosphere†

Delbert J. Eatough,* Vernon F. White, and Lee D. Hansen

Thermochemical Institute and Department of Chemistry, Brigham Young University, Provo, Utah 84602

Norman L. Eatough

Department of Chemistry, California Polytechnic State University, San Luis Obispo, California 93407

James L. Cheney

Environmental Sciences Research Laboratory, Research Triangle Park, North Carolina 27711

■ Gas-phase dimethyl sulfate and monomethyl hydrogen sulfate have been identified in the atmosphere in Los Angeles. Gas-phase concentrations of these two alkyl sulfates were determined by using analytical methods based on the collection of the compounds before collection of particles using diffusion denuders and after collection of particles using resin beds or sorption filters, and specific analysis of the collected alkyl sulfates by ion chromatography. The data show that dimethyl sulfate is present in both particles and the gas phase. The concentration of total gas-phase methyl sulfates was found to vary from 34 to 178 nmol/m^3 during the smog episode studied. These species constituted a significant fraction of the total sulfur budget in the Los Angeles basin during the sampling period.

Introduction

We have previously reported the presence of dimethyl and monomethyl sulfate in coal and oil fly ash and airborne particulate matter (*1–4*). Durham et al. (*5*) have collected a gas-phase species with a diffusion coefficient equal to that expected for methylated sulfates by a nylon denuder sampling the atmosphere in Riverside, CA. The species appeared as sulfate in ion chromatographic analysis of samples weeks to months after sample collection. They have also shown that gas-phase monomethyl hydrogen sulfate is collected by nylon denuders and, over time, is converted to sulfate. On the basis of these data they have postulated the presence of gas-phase monomethyl hydrogen sulfate and/or dimethyl sulfate in the Los Angeles basin. If the postulate is correct, their data indicate that the concentrations of gas-phase methylated sulfates are comparable to the concentration of aerosol sulfate in the atmosphere studied.

This paper is a report of the results obtained from a 3-day sampling period by using five different simultaneous sampling trains in the Los Angeles basin atmosphere. Details of the validation of the procedures used for the simultaneous collection of both dimethyl sulfate and monomethyl hydrogen sulfate in the gas phase using a variety of diffusion denuders, and filter or resin bed collection systems are reported in another paper (*6*).

Table I. Configuration of the Sampling System for the Collection of Gas-Phase Alkyl Sulfates

sampler	sample flow rate, L/min	material collected[a] gas phase	material collected[a] particles
(1) high vol sampler with quartz filters	1000		DMS, MSA
(2) nylon denuder	2.0	DMS, MSA	
+ quartz filter			DMS, MSA
+ nylon filter		DMS, MSA	
(3) paper denuder	2.0	MSA	
+ quartz filter			DMS, MSA
+ nylon filter		DMS, MSA	
(4) quartz filter	20		DMS, MSA
+ XAD-II bed		DMS	
+ nylon filter		MSA	
(5) quartz filter	20		DMS, MSA
+ nylon filter		DMS & MSA	
+ XAD-II bed		any DMS passing nylon filter	

[a] DMS is dimethyl sulfate and MSA is monomethyl hydrogen sulfate.

Experimental Section

Sampling Techniques. The configurations of the five samplers used for collection of alkyl sulfate compounds are given in Table I. The various procedures have all been tested in the laboratory using samples of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate. Details of the sampling techniques and the verification of the collection of the gas-phase species with the specificity indicated in Table I are given elsewhere (*6*). Sampler 1 is a high volume cascade impactor with a 15-μm cyclone preseparator. The inlet to the other four samplers contains two impaction plates (PIXE International) with an adhesive surface to remove particles greater in size than 3

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Table II. Comparison of Results Obtained with Various Techniques for the Determination of Gas-Phase Alkyl Sulfate Compounds in the Los Angeles Atmosphere

species	sampling system in Table I	mol of alkyl sulfate/mol of total sulfur for sampling period							
		1	2	3	4	5	6	7	8
$(CH_3O)_2SO_2$	(3) nylon filter	ND[a]	ND	0.056	0.492	0.236	0.350	0.123	0.124
	(4) XAD-II bed	0.040	0.100	0.064	0.397	0.281	0.289	0.093	0.082
CH_3OSO_3H	(3) denuder[b]	0.096	0.229	0.214	ND	0.394	ND	0.295	ND
	(3) denuder[c]	0.096	0.106	0.190	ND	0.200	0.110	0.087	ND
	(4) nylon filter	0.112	0.002	0.122	0.035	0.093	0.093	0.034	0.030
CH_3OSO_3H + $(CH_3O)_2SO_2$	(2) denuder[d]	0.131	0.137	0.328	0.523	0.603	0.342	0.218	0.200
	(2) Denuder[e]	0.112	0.063	0.129	0.266	0.311	0.330	0.141	0.135
	(3) Den + Nyl[f]	ND	ND	0.261	ND	0.630	0.460	0.418	ND
	(3) Den + Nyl[g]	ND	ND	0.194	ND	0.436	0.456	0.210	ND
	(4) XAD-II + Nyl	0.152	0.102	0.186	0.432	0.374	0.382	0.127	0.112
	(5) Nyl + XAD-II	0.022	0.089	0.232	0.270	0.172	0.440	0.056	ND

[a] ND = not determined. [b] Total sulfur on paper denuder corrected for SO_2; see text. [c] Monomethyl sulfate only on paper denuder. [d] Total sulfur on nylon denuder corrected for SO_2; see text. [e] Monomethyl sulfate only on paper denuder. [f] Total sulfur on paper denuder corrected for SO_2 (see text) plus dimethyl sulfate collected on Nylon filter. [g] Monomethyl sulfate only on paper denuder plus dimethyl sulfate collected on nylon filter.

Table III. Concentration of Various Sulfur Species Found in the Los Angeles Atmosphere

set	date	time[a]	period, h	concentrations, nmol/m^3				
				gas phase			particulate matter	
				$(CH_3O)_2SO_2$[b]	CH_3OSO_3H[c]	SO_2(g)	$(CH_3O)_2SO_2$	sulfate
1	Aug 1	11:00	8	11	29 ± 3	159	0.2	130
2	Aug 1	20:00	10	31	3 ± 6	115	<0.5	160
3	Aug 2	10:00	8	33 ± 3	95 ± 37	252	8.7	150
4	Aug 2	22:00	4	164 ± 25	14 ± 20	126	2.1	105
5	Aug 3	02:00	4	80 ± 10	34 ± 29	120	0.3	80
6	Aug 3	07:00	3	89 ± 12	21 ± 11	80	0.2	95
7	Aug 3	11:00	3	62 ± 12	15 ± 11	317	0.1	143
8	Aug 3	14:00	4	50 ± 14	21 ± 21	248	0.2	155

[a] PDT. [b] Obtained from the data from sampling systems 3 and 4, Table I; see text. [c] Obtained from all the data except that for the sampling system with a paper denuder; see text.

μm. In all cases where a nylon filter was used, a two-stage nylon filter was employed. The second filter was used to test for possible artifact formation of sulfate from SO_2(g) (*6–8*). Potassium carbonate–glycerol-saturated fast-flow filters (*9*) were used after the last collection device in configurations 1, 4, and 5 to collect SO_2(g).

Sampling. Samples from the Los Angeles basin were collected during a 3-day period in August 1983 by sampling during both the daytime and nighttime at the City of Hope Hospital in Duarte. Immediately after collection, all samples were placed in sealed containers and stored in the dark at −80 °C until analyzed.

Analysis. Particle-phase dimethyl sulfate and monomethyl sulfate were determined on the quartz filters in configurations 1, 4, and 5 (Table I) by exposure of a fraction of the collected sample to NH_3(g) to convert dimethyl sulfate to monomethyl sulfate + methylamine (*2*) followed by ion chromatographic determination of monomethyl sulfate in aqueous extracts of the exposed and unexposed portions of the sample. In this analysis, dimethyl sulfate is determined as the difference between the moromethyl sulfate in the sample exposed to NH_3 and the unexposed sample (*2*). The SO_2(g) and particulate sulfate were determined as sulfate by ion chromatographic analysis of aqueous extracts of the carbonate-saturated and quartz filters, respectively. The nylon and paper diffusion denuder samples were each divided into six 10-cm sections and aqueous extractable sulfate and monomethyl sulfate determined in each section by ion chromatography. Aqueous extractable sulfate and monomethyl sulfate were determined in both of the nylon filters included in sampling configurations 2–5. The amount of dimethyl sulfate collected by the XAD-II was determined by ion chromatographic determination of the increase in both monomethyl sulfate and sulfate resulting from the hydrolysis of aqueous-extractable dimethyl sulfate.

All aqueous extractions were done for 20 min in an ultrasonic bath. In all cases, sulfate was determined by ion chromatography using a 2.4 mM $NaCO_3$–3.0 mM $NaHCO_3$ eluent, and monomethyl sulfate was determined by using a 5.0 mM $NaHCO_3$ eluent. By use of the latter eluent, $CH_3OSO_3^-$ was separated from nitrite (*1*). The retention time was checked by spiking samples with KCH_3OSO_3 standards.

Results

The results obtained in the analyses of the various samples for the gas-phase methyl sulfates are given in Table II. The calculated concentrations of all sulfur species for each of the sampling periods are given in Table III.

The deposition of the alkyl sulfates in each diffusion denuder as a function of travel distance through the denuder permits calculation of the diffusion coefficient, D_0, of the gas being adsorbed. A plot of the log of the amount deposited in equal length sections of the denuder vs. the total time for travel of a gas from the denuder entrance to passage through that section of the denuder is linear with a slope proportional to D_0 and an intercept that is a function of D_0 and the total amount of the gas entering the tube (*6*, *10*). Since any methyl sulfate gas that passed the diffusion denuders was collected by the nylon filter after the quartz filters and denuder, the total amount of alkyl sulfates entering the denuder tube and hence the

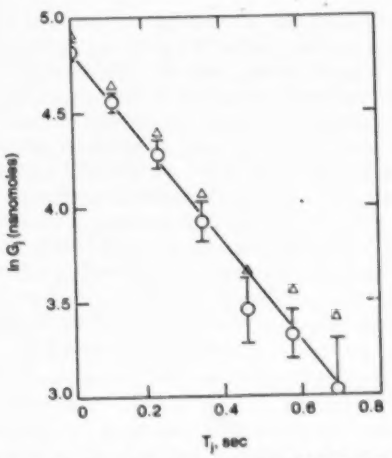

Figure 1. Plot of the ln of the amount deposited in each section of the denuder, G_j, vs. travel time through the denuder to that section, t_j, for the collection of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate by the nylon denuder (see ref 6) for sample set 3 (Table II). The (Δ) data points give the total deposited in each section. The (O) data points are corrected for the adsorption of SO_2(g); see text.

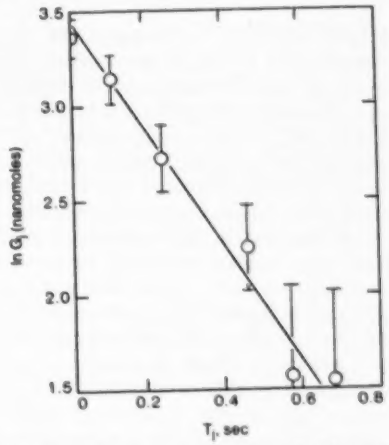

Figure 2. Plot of the ln of the amount deposited in each section of the denuder, G_j, vs. travel time through the denuder to that section, t_j, for the collection of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate by the nylon denuder (see ref 6) for sample set 6 (Table II).

intercept of the plot was determined directly.

The deposition pattern in the denuder is illustrated for the data obtained with nylon denuders for sample set 3, collected from 10:00 to 18:00 on Tuesday, August 2, 1983, and for sample set 6, collected from 7:00 to 10:00 on Wednesday, August 3, 1983.

Recent studies by us and others have shown that a small percent of the total SO_2(g) passing through nylon diffusion denuders will adsorb to the walls (*6–8*). Because the adsorption of SO_2(g) by the denuder is not quantitative and is less than 10% of the total SO_2(g) (*6–8*), the amount of SO_2(g) deposited in each section and subsequently analyzed as sulfate will be nearly constant. This will result in a positive deviation of the data on total sulfur for the last denuder sections from the line predicted based on the amount deposited in the first sections and the determined total (Figure 1). Where observed, this deviation was used to both calculate the amount of SO_2(g) adsorbed and correct for this artifact in the data by iteration. For sample set 3 (Table II), this correction is 10% of the total deposited sulfur (and 10% of the total SO_2(g)) for the six sections of the nylon denuder. This result is in agreement with the SO_2(g) adsorption determined in laboratory measurements (*6–8*) and was the maximum artifact seen in the experiments reported here. Both corrected and uncorrected deposition patterns are given in Figure 1. For the nylon diffusion denuder data in sample set 6, the deposition of SO_2(g) was not detectable (Figure 2). Sample 6 also had the lowest concentration of SO_2(g) in the ambient air (see Table III). The amount of SO_2(g) deposited in each section is a constant so the relative correction increases with distance down the denuder. The relative correction is small for the first sections and becomes a larger percent of the total collected sulfur with distance down the tube (Figure 1). The D_0 values calculated from the data shown in Figures 1 and 2 are 0.086 ± 0.008 and 0.085 ± 0.030 cm^2/s, respectively, for the sum of monomethyl hydrogen sulfate and dimethyl sulfate collected in the nylon denuders. These values are in agreement with estimated values (*5*) of D_0 of 0.081 and 0.074 cm^2/s for monomethyl sulfate and dimethyl sulfate, respectively. Similar results were obtained for each of the other nylon denuder sample sets. Similar analyses are not reported for the paper denuder because a positive artifact was sometimes present in this sampling system (see Discussion).

Discussion

Particulate Matter Alkyl Sulfates. Dimethyl sulfate was the only alkyl sulfate identified in the particulate matter collected by high-volume sampling. No monomethyl sulfate was seen in the samples before exposure to NH_3(g), thus showing that monomethyl sulfate was not present. Dimethyl sulfate was detected in all but one of the seven high-volume samples. Because of the smaller amount of material collected by the low-volume sampling systems (4 and 5, Table I) all the collected material was exposed to NH_3(g) to allow for the optimum determination of total alkyl sulfates. Alkyl sulfate was detected in only four of the seven samples collected with the low-volume sampling systems. The highest concentration of dimethyl sulfate was seen in sample set 3 (Table III). In general, the results obtained with the high-volume sampler (summed over all particle sizes) gave a lower particulate matter dimethyl sulfate concentration than the results obtained with low-volume aerosol samplers. For example, for sample set 3 the high-volume sample gave 0.013 mol of dimethyl sulfate/mol of sulfate, and the low-volume samples gave an average of 0.035 ± 0.006 mol of dimethyl sulfate/mol of sulfate. The amount of alkyl sulfate in particles is small compared to the amount in the gas phase so the observed difference between high-volume and low-volume sampling causes only a 2% uncertainty in the total alkyl sulfates measured.

Gas-Phase Alkyl Sulfates. The identification of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate as indicated in Table III is based on the following criteria: (1) The proper diffusion coefficient was observed for deposition of $(CH_3O)_2SO_2$(g) and/or CH_3OSO_3H(g) in the nylon diffusion denuder, (2) monomethyl sulfate anion, as opposed to just sulfate, was shown to be present in water extracts of the samples (see Table II), and (3) the required specificity of the various parts of the sampling system for both $(CH_3O)_2SO_2$(g) and CH_3OSO_3H(g) was observed as delineated in Table I. Each of these observations supports the presence of $(CH_3O)_2SO_2$(g) and CH_3OSO_3H(g) in the air sampled. Details of the data on which this conclusion is based are given in the following paragraphs.

(1) Nylon Diffusion Denuder Deposition Patterns. The agreement between expected and calculated D_0 values

(Figures 1 and 2) supports the identification of the species adsorbed as gas-phase dimethyl sulfate and monomethyl hydrogen sulfate. Similar results were obtained for the deposition pattern in the paper denuder when the results obtained by this system were in agreement with the other sampling techniques (see Agreement among the Various Sampling Procedures). The data cannot be explained by the deposition of either $SO_2(g)$ ($D_0 = 0.132$ cm^2/s) or other gases with D_0 greater than about 0.1 cm^2/s. Furthermore, laboratory studies on the reaction of $SO_2(g)$ in clean air have shown that SO_2 is poorly adsorbed by both the nylon (*6–8*) and the paper (*6*) denuders, and as a result, the sulfate from $SO_2(g)$ is nearly constant with distance and does not follow the Gromley–Kennedy diffusion equation.

(2) Presence of Monomethyl Sulfate in Extracts of the Samples. Identification of dimethyl sulfate and monomethyl hydrogen sulfate as the gas-phase sulfur compounds collected by the nylon denuder cannot be made just from the sulfur compounds analyzed (*6*). However, the presence of monomethyl sulfate in extracts of the samples proves that gas-phase methyl sulfates were collected by the denuder. Dimethyl sulfate reacts with the denuder to produce monomethyl sulfate as the major product, but some sulfate is also formed. Also, part of the gas-phase monomethyl hydrogen sulfate collected will react to form sulfate, while the balance will be detected as monomethyl sulfate. It is true for all sample sets that when the concentration of gas-phase dimethyl sulfate was high (Table III), the major sulfate species found in extracts of the nylon denuder sections was monomethyl sulfate (Table II). This can be illustrated by the data given in Figures 1 and 2. Figure 1 gives the SO_2-corrected deposition pattern in the nylon diffusion denuder for sample set 3. For this sample, the major sulfur-containing gas collected by the nylon diffusion denuder was $CH_3OSO_3H(g)$ (Table III). The correction for $SO_2(g)$ deposition (Figure 1) accounted for 27% of the sulfate found in the nylon denuder sections. Sulfate was the predominant product (61% of the total sulfur, corrected for $SO_2(g)$ adsorption) resulting from the adsorption of 95 nmol/m^3 monomethyl hydrogen sulfate and 33 nmol/m^3 dimethyl sulfate (Table III) by the nylon denuder. For the nylon denuder data from the sample with the lowest $SO_2(g)$ concentration (i.e., set 6, Table III) adsorption of $SO_2(g)$ was not detectable. The major gas-phase alkyl sulfate species present was dimethyl sulfate (see Table III), and the predominant sulfur compound found by ion chromatographic analysis of the water extracts of the various denuder sections was monomethyl sulfate, sulfate accounting for only 6% of the total deposited sulfur (Table II).

(3) Specificity of the Sampling System. As outlined in Table I, the various sampling systems used will collect $(CH_3O)_2SO_2(g)$ and $CH_3OSO_3H(g)$ at different points in the sampling and by different sampling chemistry. This redundancy in the sampling system provides a further check on the identification of both $(CH_3O)_2SO_2(g)$ and $CH_3OSO_3H(g)$. It should be stressed that the total data set, and not just the result from any single sampling system, proves that both gas-phase dimethyl sulfate and monomethyl hydrogen sulfate were present in the atmosphere during the sampling periods. Sampling system 2 (Table I) indicated the presence of alkyl sulfate species because monomethyl sulfate was found in the extracts of the nylon diffusion denuder sections (Table II). Equally important, the amount of total sulfur found in the nylon filters which followed the denuder sections and the quartz filter was consistent with the expected small amount of denuder breakthrough. Sampling system 3 (Table I) indicated the presence of $CH_3OSO_3H(g)$ because monomethyl sulfate was found in the extracts of the paper diffusion denuder sections (Table II). In addition, for the data obtained with sampling system 3, substantial $CH_3OSO_3^-$ (formed by adsorption of $(CH_3O)_2SO_2$) was detected on the nylon filters, consistent with the expected lack of collection of the dialkyl sulfate by the paper diffusion denuder. For the data obtained with sampling system 4, evidence for dimethyl sulfate was seen in the expected slow hydrolysis of dimethyl sulfate after extraction of the XAD-II bed with water. Neither monomethyl sulfate nor sulfate (above the sulfate blank values) was detected immediately after extraction of the XAD-II with water. After the extract solutions stood overnight, both sulfate and monomethyl sulfate were found. In laboratory studies with pure dimethyl sulfate, monomethyl sulfate was the only hydrolysis product (*6*); however, the results reported here are consistent with results previously reported for the hydrolysis of dimethyl sulfate after extraction of environmental samples (*2*, *3*). Monomethyl hydrogen sulfate is not collected by the XAD-II (*6*). Monomethyl sulfate was always found on the first nylon filter after the XAD-II bed, verifying the presence of gas-phase monomethyl sulfate. Finally in configuration 5, with the exception of sample sets 4 and 6 where 18 and 9%, respectively, of the total alkyl sulfate was found on the XAD-II bed after the nylon filters, no evidence for dimethyl sulfate on the XAD-II bed after the nylon filters was seen, as expected. Thus, the required specificity in the data set was satisfied.

Agreement among the Various Sampling Procedures. Gas-phase dimethyl sulfate was separated from gas-phase monomethyl hydrogen sulfate by two systems. The nylon filter in sampler 3 (Table I) collects dimethyl sulfate after removal of monomethyl sulfate by the paper diffusion denuder. The XAD-II resin bed after the quartz filter in sampler 4 selectively collects dimethyl sulfate in the presence of gas-phase monomethyl sulfate. The results obtained by using these two different collection techniques are in good agreement (Table II). Linear regression analysis of the results obtained by the two techniques gives $r^2 = 0.92$, a slope of 0.81 ± 0.11, and an intercept of 0.01 ± 0.04, compared to the expected values of the slope and intercept of 1.00 and 0.00, respectively. The slope indicates that the values obtained for the concentration of $(CH_3O)_2SO_2(g)$ by the nylon filter after the paper denuder (sampler 3 in Table I) were, on the average, 19% higher than the concentrations obtained with the XAD-II resin after the quartz filter (sampler 4 in Table I).

Agreement between the two techniques for selective collection of gas-phase monomethyl hydrogen sulfate was not good (Table II). Monomethyl hydrogen sulfate was separated from dimethyl sulfate and collected by the paper diffusion denuder and also by the nylon filter placed after an XAD-II sorption bed. Linear regression analysis of these two data sets gives $r^2 = -0.07$ with a slope of -0.11 ± 0.20 and an intercept of 0.10 ± 0.05. When the results were in poor agreement, the value obtained with the paper denuder system was high. It is not possible to determine which of the values is the better number from these results alone. Two explanations for the disagreement are possible. (1) The concentration of $CH_3SO_3H(g)$ determined from the paper denuder system may be high, possibly because the correction for the adsorption of $SO_2(g)$ was inadequate, because other gas-phase organosulfur compounds were collected by the paper denuder and subsequently determined as sulfate, or because sulfur in the paper was converted to sulfate during the sampling. (2) The concentration of $CH_3SO_3H(g)$ determined from the nylon filter

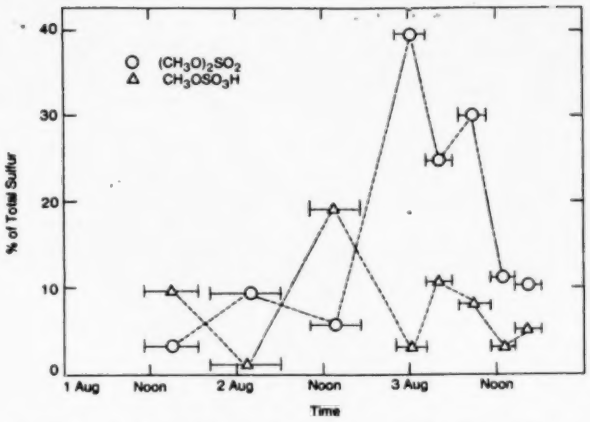

Figure 3. Variation of the mole fraction of total sulfur existing as gas-phase dimethyl sulfate (O) and gas-phase monomethyl hydrogen sulfate (Δ) as a function of sampling time; see Table III.

after the XAD-II bed may be low because $CH_3SO_3H(g)$ is not quantitatively collected by the nylon filter. The latter hypothesis does not agree with laboratory experiments which show that $CH_3OSO_3H(g)$ is efficiently collected by nylon (*6*).

Total gas-phase alkyl sulfates were determined by four different procedures. Linear regression analysis of the various results for total alkyl sulfates vs. the total calculated from the average value for $(CH_3O)_2SO_2(g)$ and either of the two methods for independently determining $CH_3OSO_3H(g)$ were done. The results indicate that the determination of CH_3OSO_3H with the paper denuder system is not in agreement with any of the other techniques. This provides additional evidence that some positive artifact is present in some of the samples with the paper diffusion denuder which results in artifact sulfate on this denuder. In contrast, the results obtained by all the other techniques are in reasonable agreement. The linear regression analyses give $r^2 = 0.67$, 0.63, and 0.59, slope = 0.98 ± 0.28, 0.78 ± 0.24, and 0.73 ± 0.28, and intercept = 0.07 ± 0.11, 0.08 ± 0.09, and −0.01 ± 0.10, for comparison with the total obtained by sampling systems 2, 4, and 5 (Table I), respectively.

The results obtained from all the linear regression analyses indicate that, within an average error of 18%, the results obtained by any configuration of the nylon denuder, nylon filter, and XAD-II sampling systems are in good agreement. The paper denuder system frequently gives results that are high when used to collect alkyl sulfates from the ambient environment. For the other systems the results were in good agreement, with the results obtained with the XAD-II bed being slightly lower than those obtained with nylon which is not preceded by XAD. Considering the many possible reactions that alkyl sulfates can undergo in the atmosphere (e.g., hydrolysis, methylation, etc.), the agreement among the various sampling systems containing nylon and XAD is very good.

Concentrations of Sulfur Compounds Determined in the Study. The concentrations of the sulfur compounds determined in the Los Angeles atmosphere for the various sampling periods are summarized in Table III. It is known from previous studies that particulate-phase organic sulfones (*12–14*) are often present at concentrations comparable to the aerosol sulfate. These compounds would be determined as particulate sulfate by the analyses done in this study. The results given in Table III indicate that the sum of gas-phase dimethyl sulfate and monomethyl hydrogen sulfate accounts for 11–43% of the total sulfur in the collected samples. The variation in the contribution of each of these two species to the total sulfur with time is shown in Figure 3.

No data from atmospheric studies presently exist that can be used to determine the mechanism for formation of either dimethyl sulfate or monomethyl sulfate in the atmosphere. Previously reported studies using nylon (*5, 11*) and activated charcoal (*15*) denuders suggest that high concentrations of alkyl sulfates may be common in urban atmospheres. The data in Figure 3 suggest that monomethyl sulfate may be the dominant alkyl sulfate formed from reactions in the daytime. This may result either from the direct formation of monomethyl hydrogen sulfate or from the formation of dimethyl sulfate, followed by decomposition of this compound to monomethyl hydrogen sulfate. The results given in Figure 3 indicate that dimethyl sulfate may be more stable in the nighttime than in the daytime. The high percentage of total sulfur present as dimethyl sulfate in the sample collected between 22:00 August 2–2:00 August 3 indicates that some mechanism must exist for the formation of dimethyl sulfate in the night. The known mutagenic effects of dimethyl sulfate (*16, 17*) indicate that more data on the formation mechanism(s) and atmospheric concentrations of alkyl sulfates are needed.

Acknowledgments

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Registry No. $(CH_3O)_2SO_2$, 77-78-1; CH_3OSO_3H, 75-93-4.

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